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Synthesis of a Phosphapyracene via Metal-Mediated Cyclization: Structural and Reactivity Effects of Acenaphthene Precursors

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Ge Wang, [a] Marites A. Guino-o,[a] David S. Glueck,[a]* James A. Golen,[b] Christopher J. A. Daley, [b] and Arnold L. Rheingold[b]

Metal-mediated synthesis of a new heterocycle, 1-phenyl-phosphapyracene (**Ph-4**, Ph-PyraPhos), by tandem phosphination/cyclization of *peri*-substituted 5-bromo-6-chloromethylacenaphthene (**3**) was investigated for comparison to Pt-catalyzed formation of 1-phosphaacenaphthenes (**2**, AcePhos) from the analogous naphthalene precursor (**1**). Reaction of PH_2Ph with **3**, $NaOSiMe_3$ and a Cu catalyst gave **Ph-4**; a Pt catalyst yielded $PHPh(CH_2Ar)$ (**Ph-11**, Ar = 5-Br-acenaphthyl). Deprotonation of a complex of this secondary phosphine, [Pt((*R,R*)-Me-DuPhos)(Ph)($PHPh(CH_2Ar)$)][PF_6] (**17**), generated the phosphido intermediate Pt((*R,R*)-Me-DuPhos)(Ph)($PPhCH_2Ar$) (**Ph-8**), which cyclized to give [Pt((*R,R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][PF_6] (**18**). Treatment of **Ph-8** with silver triflate gave **18** and the cyclometalated phosphine complex [Pt((*R,R*)-Me-DuPhos)(κ^2-(P,C)-5-Ph_2PCH_2-6-$C_{12}H_8$)][PF_6] (**21**), which might form via Pt(IV) intermediates. The effects of the added "ace" bridge on structure and reactivity are discussed.

Introduction

We recently reported platinum-catalyzed asymmetric tandem phosphination/cyclization of naphthalene **1** to give a new family of heterocycles, the 1-phosphaacenaphthenes (AcePhos, **2**, Scheme 1).[1] Such rigid P-stereogenic phospholanes are potentially useful as ligands in asymmetric catalysis.[2] However, further development of this catalytic process was limited because preparation of precursor **1** proceeded in low yield and was difficult to scale up,[3] or required environmentally unacceptable organomercury intermediates.[4]

We planned to address this problem by replacing naphthalene **1** with acenaphthene **3** to yield new heterocycles, the 1-phosphapyracenes (PyraPhos, **4**; Scheme 1). This was expected to make the synthesis more convenient, because 5,6-dibromoacenaphthene, a logical precursor to **3**, has been prepared from cheap acenaphthene on 400 g scale.[5]

However, literature precedent suggested that the formal addition of a two-carbon "ace" bridge in **3** vs **1** might adversely affect the desired reactivity. Steric strain in naphthalenes may be relieved by increasing the *peri*-distance between the 1- and 8-substituents, placing these groups on opposite sides of the naphthalene plane, and by distorting the ring.[6] Adding the "ace" bridge in acenaphthene clamps the *peri* substituents together, which commonly increases the *peri*-distance on the other side of the naphthalene.[7] This perturbation can have striking structural effects, such as the difference between a Lewis acid-base adduct in naphthalene **5** and a frustrated Lewis pair in acenaphthene **6** (Chart 1).[8] Similarly, we hypothesized that P-C bond formation in proposed acenaphthene intermediate **8** would be slower than that in naphthalene **7** because the added bridge would increase the separation between the phosphido and aryl bromide groups and make the structure less flexible (Scheme 1).[9,10]

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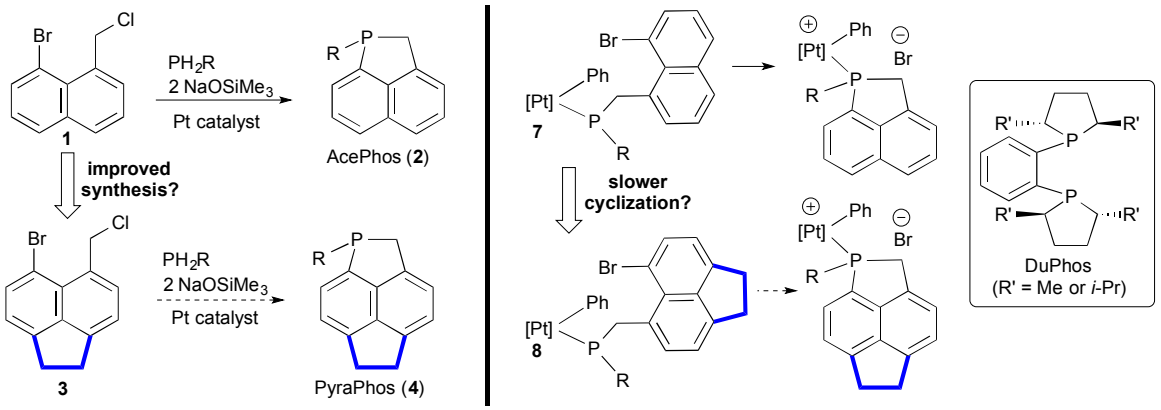
Scheme 1. Proposed effects of replacing naphthalene **1** with acenaphthene **3** in Pt-catalyzed asymmetric synthesis of P-stereogenic heterocycles: improved precursor synthesis, but slower cyclization of Pt-phosphido intermediate **8** ([Pt] = Pt(DuPhos); the "ace" bridge is highlighted in blue)



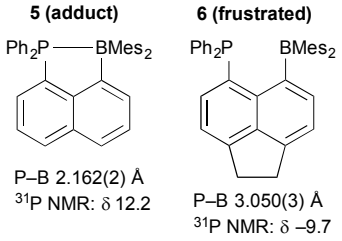


Chart 1. Structural effect of naphthalene vs acenaphthene scaffolds in a phosphine borane (Mes = mesityl)[8]

We report here that acenaphthene precursor **3** could indeed be prepared more conveniently than naphthalene **1**. As anticipated, this structural change slowed cyclization, enabling observation of proposed phosphido intermediate **8** and its conversion to a PyraPhos complex. Although Pt-catalyzed phosphination/cyclization was not successful, a simple copper catalyst converted **3** to the target PyraPhos ring system.

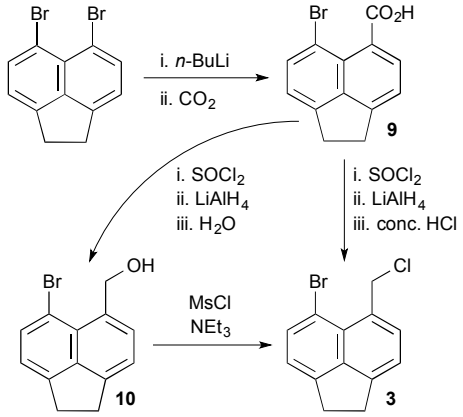
Results and discussion

Synthesis and Structure of Acenaphthene 3 and Its Derivatives

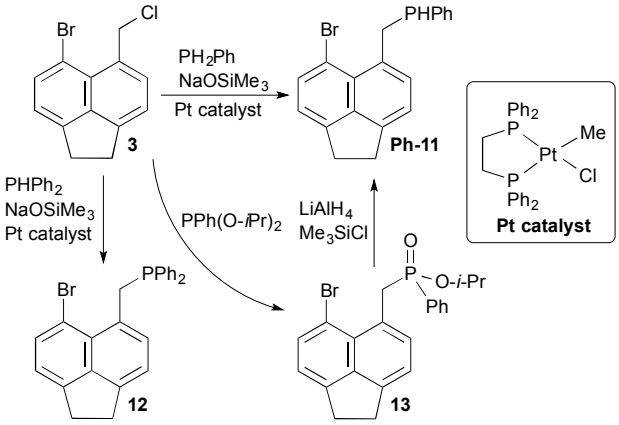
In a one-pot procedure, sequential treatment of the known[11] carboxylic acid **9** with $SOCl_2$, $LiAlH_4$, and concentrated HCl gave benzyl chloride **3**, whose ^1H and ^{13}C NMR spectra were similar to those of **1**.[1] Alternatively, aqueous workup of the $LiAlH_4$ reduction yielded alcohol **10**, which reacted with mesyl chloride and NEt_3 in CH_2Cl_2 to form **3** (Scheme 2).[1]

Pt-catalyzed phosphination of benzyl chloride **3** with PH_2Ph or $PHPh_2$ gave secondary and tertiary phosphines **Ph-11** and **12**, respectively,[12,13] while an Arbuzov reaction[14] yielded phosphine oxide **13**, which could be reduced to **11** with $LiAlH_4/SiMe_3Cl$ (Scheme 3).[15]

Scheme 2 Synthesis of Benzyl Chloride **3**



Scheme 3 Phosphination of Benzyl Chloride **3**



Comparison of the crystal structures of the acenaphthenes **3**, **Ph-11**, and **13** to those of **1** and related naphthalenes (see Figures 1-2, Table 1, and the ESI) revealed the expected

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differences, as described in the introduction. In particular, the *peri*-distances (C1-Br) increased slightly in the acenaphthenes, as the added "ace" bridge reduced the "bottom" CCC' angle and increased the "top" CCC one (Table 1).

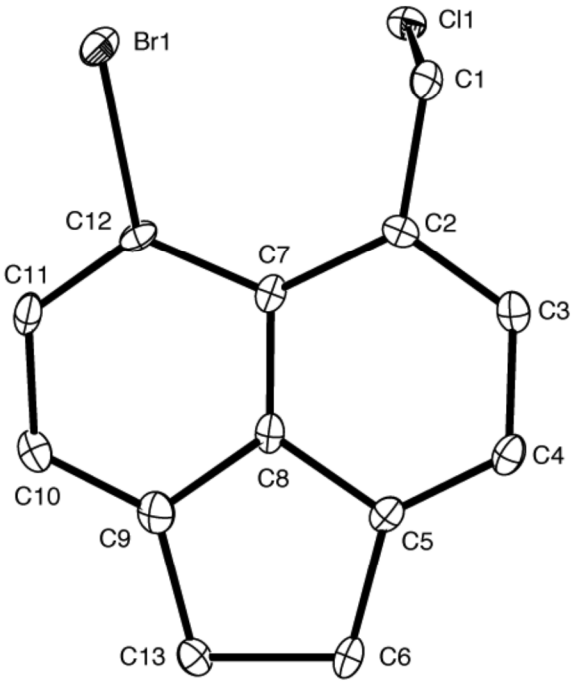

Figure 1. ORTEP diagram of acenaphthene **3**

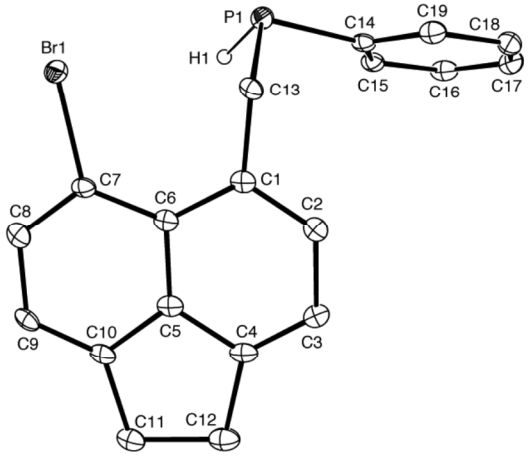

Figure 2 ORTEP diagram of the secondary phosphine **Ph-11**. Except for the P-H, which was located and refined, hydrogen atoms are not shown.

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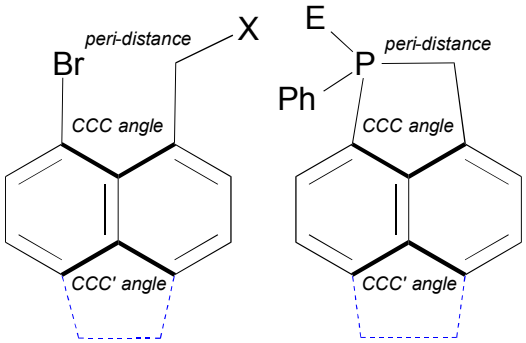
Table 1. Selected Structural Data for Naphthalene and Acenaphthene Derivatives[a]



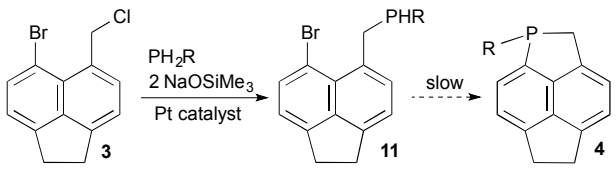
Type[b]	X or E (#)	CCC angle	CCC' angle	Displacement[c]	*peri*-distance
N	X = Cl (**1**)[d]	128.1(3)	118.2(3)	0.145, –0.175	3.156
A	X = Cl (**3**)	130.6(5)	110.4(6)	0.097, –0.15	3.238
N	X = PHPh(BH_3)[e]	128.4(3)	118.9(3)	0.073, –0.11	3.172
A	X = PHPh (**Ph-11**)	131.1(3)	111.2(3)	0.16, –0.15	3.22
A	X = PPh(O)(O-*i*-Pr) (**13**)	131.8(3)	111.1(2)	0.52, –0.45	3.255
A	X = PPh(BH_3) (**15**)[f]	131.5(3)	110.5(3)	0.048, 0.13 0.27, –0.12	3.249
A	X = [PPh_2(Pt(Me-DuPhos))]$^+$ (**21**)[g]	128.7(7)	112.2(7)	0.63, –0.23	3.272
N	E = BH_3 [h]	117.3(2)	125.3(3)	0.025, –0.065	1.852(3)
A	E = BH_3 (**14**) [i]	122.0(8)	114.3(8)	–0.048, 0.46 –0.045, -0.10	1.851(8)
A	E = O•0.5H_2O_2 (**16**•0.5H_2O_2)	120.42(2)	115.01(12)	0.24, 0.04	1.8445(13)
A	E = [Pt(Me-DuPhos)(Ph)]$^+$ (**18a**)	120.8(3)	115.5(3)	0.094, 0.11	1.861(3)

[a] Distances in Å, angles in degrees [b] N = naphthalene, A = acenaphthene [c] Displacement of the *peri*-substituents (either Br and C, or P and C) from the naphthalene or acenaphthene plane. Plus and minus signs indicate displacement on opposite sides of the naphthalene (acenaphthene) plane. Average values are reported, except in some cases where displacements differed significantly for the two molecules in the unit cell, or where there are two acenaphthyl groups in **15** [d] Average values for the two molecules in the unit cell [e] Ref 1 [f] average values for the two bromoacenaphthenyl groups, except for the displacements [g] Chelate complex; bromide was replaced by [Pt(Me-DuPhos)(PPh_2CH_2Ar)]$^+$. Displacements are reported for Pt and C, respectively. [h] Average values for the two molecules in the unit cell (Ref 1) [i] Average values for the two enantiomeric forms in the disordered crystal, except for the displacements.

Metal-Mediated Phosphination and Cyclization of 3: Synthesis and Structure of Ph-PyraPhos Derivatives

Despite these small structural changes, and the spectroscopic similarity between naphthalene and acenaphthene derivatives **1** and **3**, the one-pot Pt-catalyzed tandem process which smoothly converted **1** to AcePhos **2** was much slower for **3**, consistent with the structural hypothesis of Scheme 1. With a variety of primary phosphines, this reaction gave mostly the expected intermediate secondary phosphine **11** and little of PyraPhos **4** (Scheme 4; see the ESI for details).

Scheme 4. Attempted Pt-Catalyzed Tandem Phosphination/Cyclization of **3** (Catalyst Precursor = Pt((*R,R*)-Me-DuPhos)(Ph)(Cl))



In contrast, conversion of **3** to Ph-PyraPhos (**Ph-4**) proceeded smoothly with PH_2Ph, $NaOSiMe_3$ and the catalyst precursor CuCl, via the intermediate secondary phosphine **Ph-11** (Scheme 5).[16] After addition of BH_3(THF), Ph-

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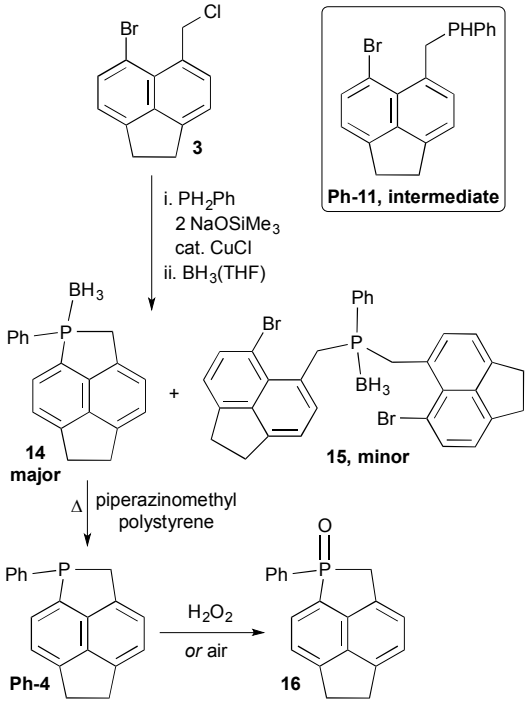
PyraPhos(BH_3) (**14**, Figure 3 and Table 1) was isolated in 76% yield after chromatographic separation from a minor (<5%) byproduct, the tertiary phosphine-borane **15** (Figure 4; see Table 1 for structural comparison to other acenaphthene derivatives). Deprotection of **14** using an amine-functionalized polymer gave pure **Ph-4**,[17] which was oxidized slowly by air to yield the phosphine oxide **16**. Faster oxidation with hydrogen peroxide gave a hydrogen-bonded H_2O_2 adduct, from which H_2O_2 could be removed with molecular sieves (see the ESI for details).[18] Although the ^{31}P NMR chemical shifts of precursors **Ph-11** and its naphthalene analogue were identical, those of Ph-PyraPhos (**Ph-4**, δ –5.6) and Ph-AcePhos (**Ph-2**, δ –15.1) were somewhat different, as also observed for their borane adducts (δ 35.8 and 28.8, respectively).[1]

Scheme 5. Copper-catalyzed Tandem Phosphination/Cyclization of **3**



The structures of **14** and **16**•0.5H_2O_2 (ESI) were similar to that of the previously characterized phosphaacenaphthene analogue, Ph-AcePhos(BH_3) (Table 1).[1] As expected, P–C bond formation resulted in drastically shorter *peri*-distances, and reduced displacement of these substituents from the acenaphthene plane.

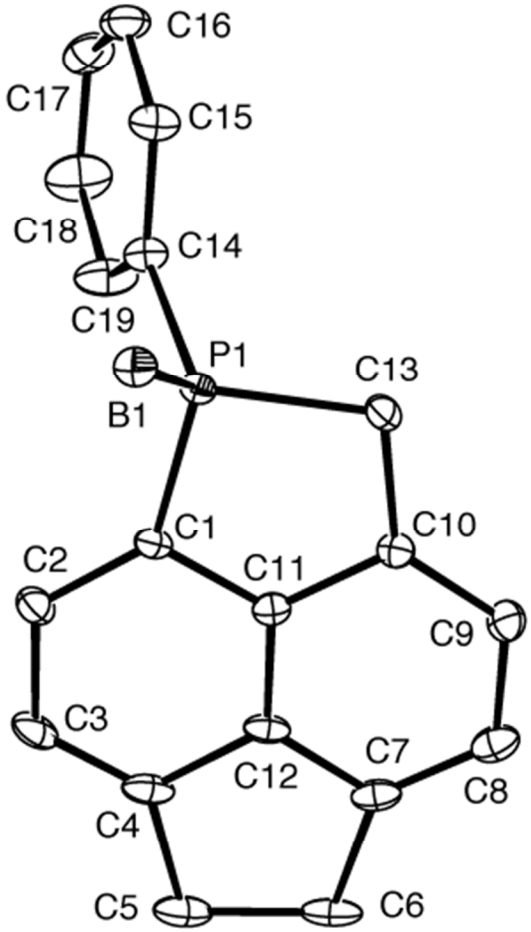


Figure 3. ORTEP diagram of Ph-PyraPhos(BH_3) (**14**). The crystal was disordered, with both enantiomers appearing in an 80:20 ratio. The major form is shown in the figure. The disorder does not represent the enantiopurity of the compound; the sample was racemic as determined from the centrosymmetric space group solution.

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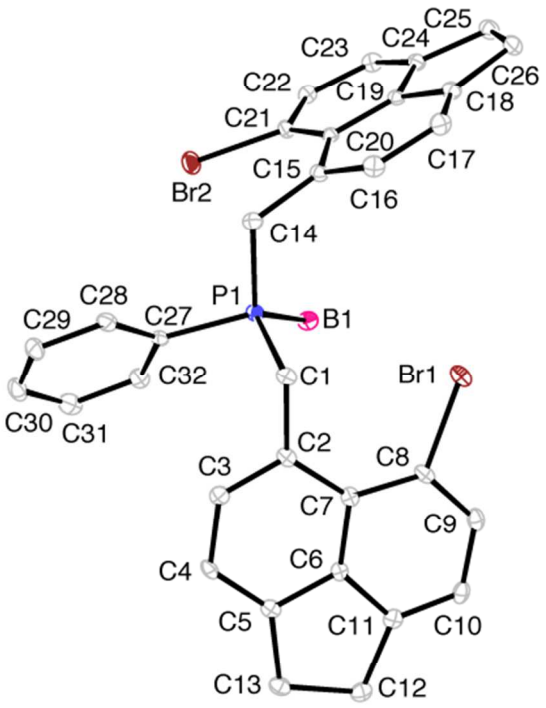
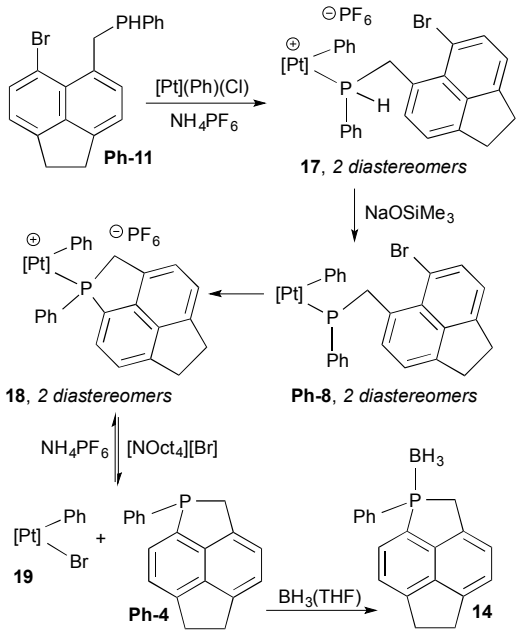


Figure 4. ORTEP diagram of tertiary phosphine-borane **15**

Platinum-Mediated Formation of Ph-PyraPhos Ph-4 via Cyclization of Phosphido Complex Ph-8

To investigate the slow Pt-catalyzed synthesis of PyraPhos derivatives, we sought to generate the proposed Pt-phosphido intermediate (**8**, Scheme 1) and to observe the cyclization step directly. Treatment of Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) with secondary phosphine **Ph-11** and NH_4PF_6 gave cation **17** as a 1.5:1 mixture of diastereomers.[19] Deprotonation of **17** with $NaOSiMe_3$ generated phosphido complex **Ph-8** as a ca. 2:1 mixture of diastereomers, consistent with the hypothesis that adding the "ace" bridge would slow ring formation (the related Pt(*i*-Pr-DuPhos) intermediate **Ph-7** had not been observed in the naphthalene series). Cyclization of **Ph-8** occurred at room temperature to give an apparent equilibrium mixture of cationic Ph-PyraPhos complex **18** (two diastereomers in ratios varying from 1.4:1 to 5:1), Ph-PyraPhos **Ph-4**, and the known Pt-Br complex **19** (Scheme 6).[20] These products always formed over multiple experiments using different batches of **17**, but the rate of cyclization and the ratio of diastereomers **18a**/**18b** was erratic and poorly reproducible, and we have not been able to discover the reason(s) for this variability (see the ESI). Adding NH_4PF_6 to the product mixture promoted Ph-PyraPhos complexation to give **18**. Alternatively, treatment with excess $[NOct_4][Br]$ shifted the equilibrium to favor Pt-bromide complex **19** and Ph-PyraPhos (**Ph-4**), which was isolated after addition of BH_3(THF) as the borane complex **14** (Scheme 6).

Scheme 6 Formation of Cationic Ph-PyraPhos Complex **18** via Cyclization of Phosphido Intermediate **Ph-8** ([Pt] = Pt((*R,R*)-Me-DuPhos))



The major diastereomer **18a** was isolated by recrystallization, and X-ray crystallography showed it contained *R*-Ph-PyraPhos (Figure 5). Replacing BH_3 in **14** with the bulky Pt-substituent had little effect on the structure of the PyraPhos group in **18a** (Table 1).

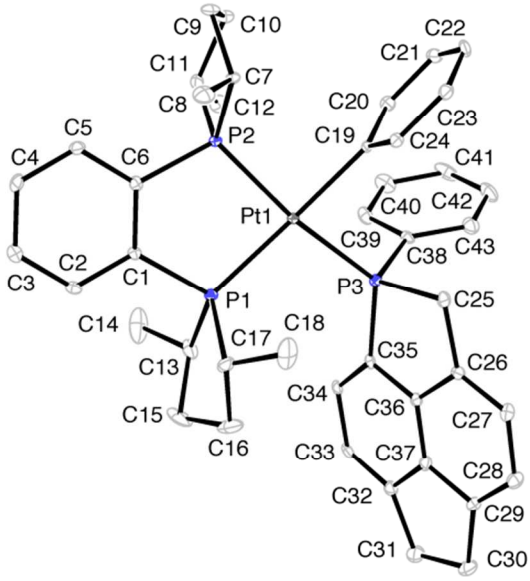


Figure 5. ORTEP diagram of [Pt((*R,R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][PF_6] (**18a**). The anion is not shown.

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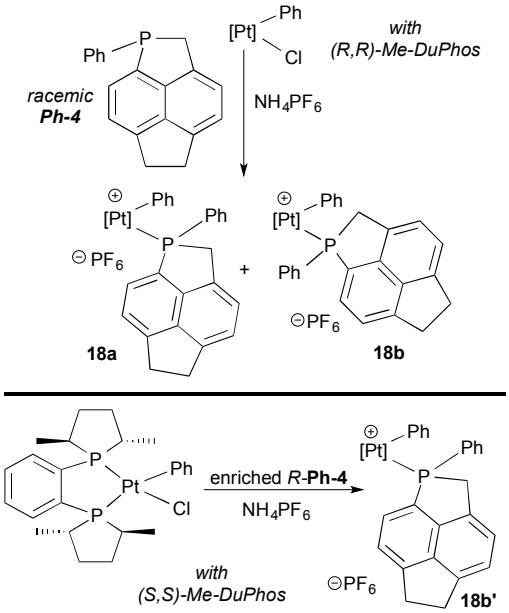
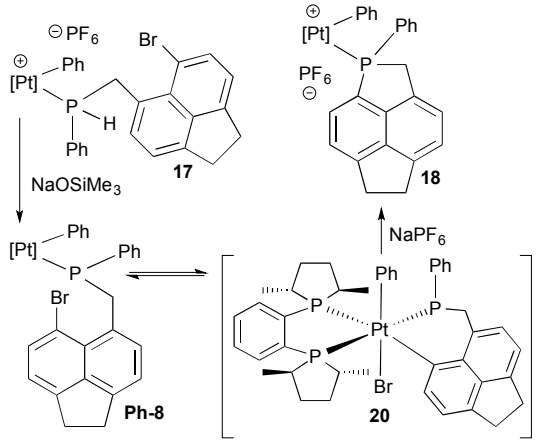
Cation **18** was prepared independently as a 1:1 mixture of diastereomers by treatment of Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) with racemic Ph-PyraPhos (**Ph-4**) and NH_4PF_6 (Scheme 7, top). Reaction of Pt((*S,S*)-Me-DuPhos)(Ph)(Cl) with NH_4PF_6 and *R*-Ph-PyraPhos (isolated after liberation from highly diastereoenriched **18a**; see the ESI) gave [Pt((*S,S*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][PF_6] (**18b'**), the enantiomer of **18b** (Scheme 7, bottom), so that highly enriched samples of both diastereomers could be characterized spectroscopically.

Scheme 7 Synthesis of Ph-PyraPhos Complex **18** By Complexation of Ph-PyraPhos **Ph-4** ([Pt] = Pt((*R,R*)-Me-DuPhos) (top) or Pt((*S,S*)-Me-DuPhos) (bottom))

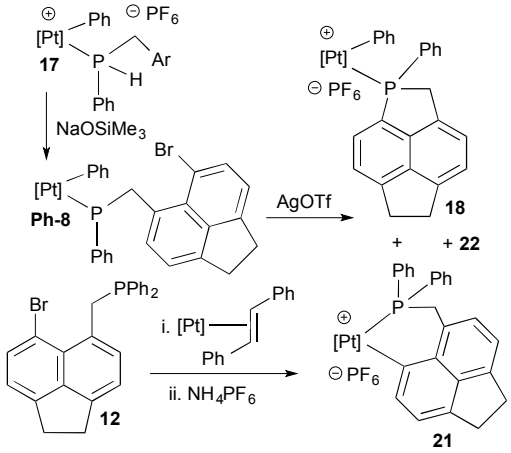


Cyclization of phosphido intermediate **Ph-8** might proceed by C–Br oxidative addition to yield octahedral Pt(IV) complex **20**. P–C reductive elimination, following dissociation of bromide, would then form Pt-Ph-PyraPhos cation **18**, in which the PF_6^- anion is derived from precursor **17** (Scheme 8).[21] To test this hypothesis, we added a silver salt to abstract bromide from putative intermediate **20**. Treatment of a yellow THF solution of phosphido intermediate **Ph-8** with silver triflate resulted in immediate darkening of the reaction mixture, followed by formation of a precipitate. Complex **Ph-8** was immediately converted to unidentified long-lived intermediates, which over a few days formed a mixture of cyclometalated **21** (major product), Ph-PyraPhos complex **18** and another unidentified [Pt(Me-DuPhos)(phosphine)(X)]$^+$ cation (**22**; Scheme 9, see the Experimental section and ESI for details).

Scheme 8. Possible Mechanism for Cyclization of Pt-phosphido Complex **Ph-8** ([Pt] = Pt((*R,R*)-Me-DuPhos))



Scheme 9. Reaction of Pt-Phosphido Complex **Ph-8** with Silver Triflate Gave a Mixture of Products, Including Cyclometalated **21**, Which Was Prepared Independently by Oxidative Addition of Bifunctional Phosphine **12** to Pt(0) ([Pt] = Pt((*R,R*)-Me-DuPhos))



The structure of **21** was confirmed by independent synthesis (Scheme 9). Oxidative addition of phosphine-functionalized aryl bromide **12** to Pt((*R,R*)-Me-DuPhos)(*trans*-stilbene),[22] followed by anion exchange with NH_4PF_6, gave **21**, whose crystal structure (Figure 6, Table 1, and ESI) confirmed the cyclometalation and the presence of the PPh_2 group. The acenaphthene ring in **21** was structurally similar to the analogues in Table 1, with larger displacements of the bulky *peri*-substituents to opposite sides of the ring. The acenaphthene also showed small distortions from planarity, ranging from 0.16 Å (C19) to –0.14 Å (C30). Although the role of AgOTf in the selectivity of cyclization of **Ph-8** is unclear, both cations **21** and **18** could form from Pt(IV) intermediates as in Scheme 8.

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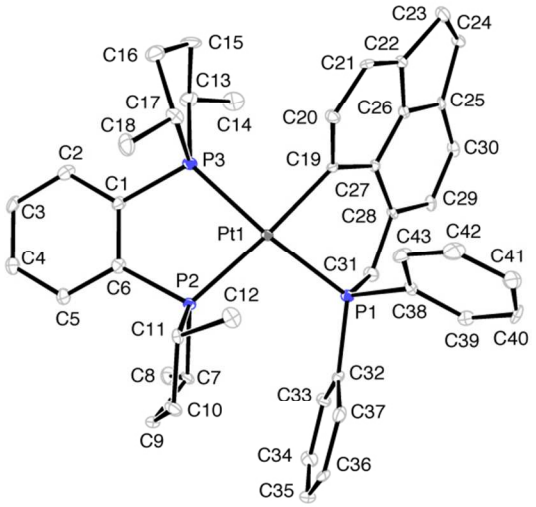

Figure 6. ORTEP diagram of the cation in [Pt((*R,R*)-Me-DuPhos)(κ^2-(P,C)-5-PPh_2CH_2-6-$C_{12}H_8$)][PF_6] (**21**). The anion is not shown.

Conclusions

As expected, the synthesis of acenaphthene precursor **3** was more convenient than that of naphthalene **1**. We hypothesized that the added "ace" bridge would slow ring formation, but were surprised by the large effect of this small structural change, which enabled observation of Pt-phosphido intermediate **Ph-8** and its cyclization to **18**. While this drastic change in reactivity precluded Pt-catalyzed reactions, copper-catalyzed tandem phosphination/cyclization yielded the desired heterocycle, Ph-PyraPhos (**Ph-4**). We hope to apply these observations to develop copper-catalyzed *asymmetric* synthesis of PyraPhos derivatives.[23]

Experimental

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at ambient temperature in a dry box or using standard Schlenk techniques. Petroleum ether (bp 38-53 °C), CH_2Cl_2, ether, THF, and toluene were dried over alumina columns similar to those described by Grubbs.[24] NMR spectra were recorded by using 300, 500 or 600 MHz spectrometers. ^1H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz, as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. Quantitative Technologies Incorporated provided elemental analyses. Mass spectrometry was performed at the University of Illinois. Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by literature methods or their modifications (ESI): 5,6-dibromoacenaphthene,[5] 6-bromo-5-acenaphthoic acid (**9**),[25,11] Pt((*R,R*)-Me-Duphos)(Ph)(Cl) and Pt((*S,S*)-Me-Duphos)(Ph)(Cl),[26] Pt(dppe)(Me)(Cl),[27] and Pt((*R,R*)-Me-Duphos)(*trans*-stilbene).[22]

Benzyl chloride 3 was prepared by a modification of the procedure reported for the naphthalene derivative.[4a] Under N_2, $SOCl_2$ (6.73 mL, 92.5 mmol, 12 equiv) was added via a syringe to carboxylic acid **9** (2.136 g, 7.71 mmol). The mixture was heated to reflux with stirring at 70 °C for 3 h; the solid dissolved to give a deep green solution. After cooling to room temperature, the excess $SOCl_2$ was removed under vacuum to give a grey solid, which was dissolved in 150 mL of ether. Under positive N_2 flow, solid $LiAlH_4$ (322 mg, 8.47 mmol, 1.1 equiv) was added to give a white suspension, which was refluxed at 33 °C for 36 h. The flask was cooled in an ice-water bath, and 15 mL of conc HCl was added dropwise. The mixture was stirred overnight, then filtered through Celite. The organic layer was separated and washed with water, aqueous $NaHCO_3$, and water again, then dried with $MgSO_4$. Removal of the solvent with a rotary evaporator gave the crude product as a white solid. Recrystallization from ether gave 1.026 g of pure white crystals (47% yield).

Anal. Calcd. for $C_{13}H_{10}BrCl$: C, 55.45; H, 3.58; Found C, 55.54; H, 3.57. HRMS m/z calcd for $C_{13}H_{10}BrCl$: 279.9654. Found: m/z 279.9652. ^1H NMR ($CDCl_3$): δ 7.79 (d, J = 7, 1H), 7.57 (d, J = 7, 1H), 7.28 (d, J = 7, 1H), 7.15 (d, J = 7, 1H), 5.48 (2H), 3.36 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.1, 147.1, 141.9, 135.3, 133.9, 129.9, 128.3, 121.0, 120.2, 113.6, 46.3, 30.5, 30.2.

Secondary Phosphine Ph-11 A solution of PH_2Ph (0.028 g, 0.25 mmol, 1 equiv) in 1 mL of THF was added to a mixture of $NaOSiMe_3$ (0.055 g, 0.50 mmol, 2 equiv in 1 mL of THF; note, this excess of base was not required, and 1 equiv also worked well) and Pt(dppe)(Me)(Cl) (0.008 g, 0.01 mmol, 0.05 equiv in 1 mL of THF) resulting in a light yellow solution. A solution of benzyl chloride **3** (0.071 g, 0.25 mmol, 1 equiv) in 1 mL of THF was added, yielding an orange solution. The mixture was stirred overnight and the solvent was removed *in vacuo*. The yellow solid was dissolved in 10 mL of 10% toluene/petroleum ether and the solution was filtered through a silica plug, which was washed with 20-40 mL of the solvent mixture. Removing the solvent from the filtrate *in vacuo* gave a white solid (0.080 g, 89% yield). Alternatively, the solid residue was extracted with 5-10 mL of ether, and the solution was filtered through Celite to give a clear yellow solution, which was cooled to –25 °C in a refrigerator. A white precipitate formed after one day. The solvent was decanted and the white solid was dried *in vacuo* to give spectroscopically pure product.

Elemental analysis was consistent with oxidation of the air-sensitive phosphine. Anal. Calcd. for $C_{19}H_{16}BrP$: C, 64.24; H, 4.54; Anal. Calcd. for $C_{19}H_{16}BrOP$: C, 61.48; H, 4.34.

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Found: C, 61.18; H, 4.02. HRMS m/z calcd for $C_{19}H_{16}BrP$: 355.0251. Found: m/z 355.0254. ^{31}P NMR (C_6D_6): δ –36.2 (d, J = 210). ^{31}P NMR ($CDCl_3$): δ –37.0 (d, J = 214). ^{1}H NMR (C_6D_6): δ 8.03-8.02 (d, J = 7, 1H), 7.73-7.69 (m, 2H), 7.56 (1H), 7.48-7.41 (m, 4H), 7.03-7.01 (dt, J = 2, 7, 1H), 5.14-5.11, 4.78-4.69, 4.17-4.13 (m, PH and CH_2, 3H), 3.22-3.12 (m, 4H). ^{1}H NMR ($CDCl_3$): δ 7.71-7.70 (dd, J = 2, 7, 1H), 7.37-7.24 (m, 3H), 7.07-7.02 (m, J = 7, 21, 3H), 6.86-6.85 (m, 2H), 4.32 (dt, J = 6, 214, PH, 1H), 4.26-4.21 (m, 1H), 3.77-3.73 (m, 1H), 3.30 (4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 147.0, 145.3 (d, J = 2), 141.9, 135.3 (d, J = 13), 134.31, 134.3 (d, J = 3), 131.75, 131.71, 131.6, 128.2 (d, J = 4), 128.19, 120.1, 119.7 (d, J = 2), 114.1, 30.7 (d, J = 15), 30.0, 29.9.

Tertiary Phosphine 12 A solution of $PHPh_2$ (67 mg, 0.36 mmol, 1 equiv) in 1 mL of THF was added to a mixture of $NaOSiMe_3$ (44 mg, 0.39 mmol, 1.1 equiv in 1 mL of THF) and Pt(dppe)(Me)(Cl) (11 mg, 0.017 mmol, 0.05 equiv in 1 mL of THF) resulting in a yellow solution. To this mixture, a solution of benzyl chloride **3** (100 mg, 0.36 mmol, 1 equiv) in 1 mL of THF was added. Stirring at room temperature for 22 h gave a light yellow suspension. The solvent was removed under vacuum, and the light pink residue was extracted with ether (8 x 3 mL). The extract was filtered through a Celite plug to give a clear solution, which was pumped down under vacuum to give 130 mg (85% yield) of crude product as a mixture of white solid at the bottom of the vial and light yellow solid on the walls. The white solid (43 mg) was carefully separated with a spatula, and shown to be pure by NMR spectroscopy. The light yellow solid was extracted with 12 mL of ether. The extract was filtered through a Celite plug to give a clear solution which was cooled to -20 °C. A white precipitate formed after one day. The solvent was decanted and the white solid was dried under vacuum to give 54 mg of product, which contained about 8% of the phosphine oxide ($^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 29.4; this signal grew significantly after the NMR sample was exposed to air overnight). A portion of the above sample (39 mg) was dissolved in CH_2Cl_2 and passed through a silica plug to remove the phosphine oxide. After removal of the solvent, 24 mg of pure white solid was obtained (total yield = 67 mg (44%)).

Anal. Calcd for $C_{25}H_{20}BrP$: C, 69.62; H, 4.67; Found: C, 69.10; H, 4.42. HRMS (m/z): calcd for $C_{25}H_{21}BrP$ $(MH)^+$: 431.0564; found, 431.0562. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ –9.6. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, J = 7, 1H), 7.46-7.42 (m, 4H), 7.37-7.33 (m, 6H), 7.10 (d, J = 7, 1H), 6.94 (d, J = 7, 1H), 6.64 (dd, J = 3, 7, 1H), 4.35 (2H, benzyl CH_2), 3.32 (4H, ace-CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 146.8 (Ar, quat), 145.5 (d, J = 3, Ar, quat), 141.8 (d, J = 2, Ar, quat), 138.6 (d, J = 17, Ar, quat), 134.5 (Ar), 133.3 (d, J = 18, Ar), 132.3 (d, J = 8, Ar), 129.5 (d, J = 9, Ar, quat), 128.8 (d, J = 3, Ar, quat), 128.5 (Ar), 128.2 (d, J = 6, Ar), 120.1 (Ar), 119.6 (d, J = 2, Ar), 114.5 (Ar, quat), 35.3 (d, J = 15, benzyl-CH_2), 30.0 (ace-CH_2), 29.9 (ace-CH_2).

Copper-Catalyzed Reaction of Benzyl Chloride 3 with PH_2Ph and $NaOSiMe_3$ to Give Ph-PyraPhos(BH_3) (14) and $PhP(CH_2Ar)_2(BH_3)$ (15) A solution of $NaOSiMe_3$ (437 mg, 3.9 mmol, 2.2 equiv) in 2 mL of THF was added to a solution of CuCl (9 mg, 0.09 mmol, 5 mol %) in 1 mL of THF. A solution of PH_2Ph (195 mg, 1.77 mmol) in 2 mL of THF was added to the yellow mixture, which turned dark red. A solution of benzyl chloride **3** (499 mg, 1.77 mmol) in 2 mL of THF was added, giving the mixture a dark brown color. The reaction was monitored by ^{31}P NMR spectroscopy. After 20 min of stirring, ^{31}P NMR integration showed about 40% conversion of the starting primary phosphine to the intermediate secondary phosphine **Ph-11** (δ -36.9 in THF). After 2.5 h, almost all the primary phosphine was converted to secondary phosphine, and a peak due to Ph-PyraPhos **Ph-4** also appeared (δ -5.5). The reaction was done in 7 h. ^{31}P NMR signals due to impurities were observed at δ -10.2 (4%), -12.9 (1%) and -14.3 (1%). Under positive N_2 pressure, 2.7 mL of a BH_3-THF solution (1 M in THF, 2.7 mmol, 1.5 equiv) was added dropwise by syringe to the dark brown mixture, which was stirred for 2 min. The ^{31}P NMR spectrum confirmed the formation of **14** (δ 36.8, apparent d, J = 53) as well as side products (δ 23.4, 3%; δ 21.6, 2%).

Aqueous NH_4Cl (20 mL of 1 M solution) and 20 mL of ether were added slowly to the deep brown mixture, which was stirred for 5 min and filtered through Celite. The product was extracted with 2×20 mL of ether. The organic layer was collected and dried with $MgSO_4$. Removing the solvent under reduced pressure gave a sticky brown oil. This crude product was purified by chromatography on silica (R_f = 0.28 in 10:1 hexane/ethyl acetate). Since the product decomposes on the column, chromatography needs to be done quickly. The minor product **15** had similar polarity (R_f = 0.21 in 10:1 hexane/ethyl acetate). Repeated chromatography gave a total of 390 mg (76% yield) of white solid. Vapor diffusion of hexane into an ether solution at room temperature gave transparent crystals after 4 d.

Anal. Calcd for $C_{19}H_{18}PB$: C, 79.20; H, 6.30; Found: C, 78.93; H, 6.07. HRMS (m/z): calcd for $C_{19}H_{17}PB$ $(M\text{-}H)^+$, 287.1161, found, 287.1169. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 35.8 (apparent d, J = 61). ^{1}H NMR ($CDCl_3$): δ 7.73 (t, J = 7, 1H), 7.57-7.53 (m, 2H), 7.46-7.41 (m, 3H), 7.37-7.34 (m, 3H), 3.85 (AB q, J_{AB} = 18, 1H, benzyl), 3.65 (ABX, J_{AB} = 18, J_{AX} = 9, 1H, benzyl), 3.53-3.48 (m, 4H, ace H), 1.6-0.8 (m, broad, 3H, BH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.9 (d, J = 2, Ar, quat), 143.8 (Ar, quat), 138.9 (d, J = 15, Ar, quat), 138.6 (d, J = 8, Ar, quat), 132.3 (Ar, quat), 132.0 (Ar, quat), 131.9 (d, J = 10, Ar), 131.6 (d, J = 3, Ar), 129.9 (d, J = 10, Ar), 129.0 (d, J = 10, Ar), 127.3 (d, J = 57, Ar, quat), 125.4 (d, J = 7, Ar), 121.8 (d, J = 11, Ar), 121.3 (Ar), 34.8 (d, J = 40, benzyl CH_2), 32.0 (d, J = 1, ace-CH_2), 31.3 (ace-CH_2).

In a similar reaction starting with 862 mg (3.06 mmol) of benzyl chloride **3**, 15 mg (0.024 mmol, 1.6% yield) of the minor product **15** was separated through chromatography and characterized spectroscopically. Although this material

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was not obtained in analytically pure form, slow evaporation of the chromatographic eluent (20:1 hexane/ethyl acetate) gave small X-ray quality crystals.

HRMS (m/z): calcd for $C_{32}H_{26}BrPB$ $(M-H_2Br)^+$, 531.1049, found, 531.1060. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.3 (apparent d, J = 53), plus an unidentified peak at δ 20.9 (10%, apparent d, J = 71). ^1H NMR ($CDCl_3$): δ 7.64-7.60 (m, 2H), 7.57 (d, J = 8, 2H), 7.38 (dt, J = 8, 1, 1H), 7.26 (dt, J = 8, 2, 2H), 7.23 (dd, J = 8, 3, 2H), 7.09 (d, J = 7, 2H), 7.01 (d, J = 7, 2H), 4.69 (ABX, J_{AB} = 15, J_{AX} = 11, 2H, benzyl), 4.35 (ABX, J_{AB} = 15, J_{AX} = 13, 2H, benzyl), 3.34-3.26 (m, 8H, ace H), 1.2-0.2 (m, broad, 3H, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.2 (Ar, quat), 146.6 (d, J = 3, Ar, quat), 141.7 (d, J = 2, Ar, quat), 135.0 (Ar), 133.8 (d, J = 7, Ar), 133.5 (d, J = 8, Ar), 131.3 (d, J = 3, Ar), 129.4 (d, J = 4, Ar, quat), 128.8 (d, J = 48, Ar, quat), 128.4 (d, J = 9, Ar), 125.1 (d, J = 6, Ar, quat), 120.3 (Ar), 120.0 (d, J = 3, Ar), 114.2 (d, J = 1, Ar, quat), 30.3 (ace-CH_2), 30.1 (ace-CH_2), 29.8 (d, J = 31, benzyl CH_2).

Deprotection of Ph-PyraPhos(BH_3) (14) to give Ph-PyraPhos (Ph-4) A solution of phosphine-borane **14** (267 mg, 0.927 mmol) in 20 mL of toluene was added to piperazinomethyl polystyrene (1% DVB, 100-200 mesh, Matrix Innovation, 687 mg, 2.7 mmol/g, 1.85 mmol, 2 equiv) in a 50 mL Schlenk flask.[17] The mixture was stirred at 60 °C under N_2 for 2 d. The toluene was removed under reduced pressure; the residue was redissolved in THF and the insoluble polystyrene resin was filtered off. Removal of THF gave white crude product (250 mg, 98%), which contained 6% of the corresponding phosphine oxide (^{31}P NMR integration). The crude product was dissolved in CH_2Cl_2 and passed through a silica plug (5 cm long) to remove the phosphine oxide **16** (see the ESI). Removal of CH_2Cl_2 gave pure white solid (234 mg, 92%).

HRMS (m/z): calcd for $C_{19}H_{16}P$ $(MH)^+$, 275.0990, found, 275.0990. We could not obtain satisfactory elemental analysis data for the air-sensitive phosphine. Anal. Calcd for $C_{19}H_{15}P$: C, 83.20; H, 5.51. Found: C, 82.56; H, 5.84. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -5.6. ^1H NMR ($CDCl_3$): δ 7.64 (dd, J_{P-H} = 3, J_{H-H} = 7, 1H), 7.36-7.31 (m, 2H), 7.31-7.25 (m, 3H), 7.25-7.20 (m, 3H), 3.84 (ABX, J_{AB} = 17, J_{AX} = 23, 1H, benzyl), 3.50-3.44 (m, 4H, ace H), 3.41 (ABX, J_{AB} = 17, J_{AX} = 5, 1H, benzyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.4 (Ar, quat), 142.7 (Ar, quat), 141.6 (d, J = 22, Ar, quat), 139.8 (d, J = 5, Ar, quat), 139.1 (d, J = 2, Ar, quat), 137.9 (d, J = 5, Ar, quat), 137.6 (d, J = 13, Ar, quat), 131.8 (d, J = 19, Ar), 129.1 (d, J = 19, Ar), 128.8 (Ar), 128.6 (d, J = 6, Ar), 124.6 (d, J = 1, Ar), 121.0 (d, J = 5, Ar), 120.6 (d, J = 1, Ar), 35.8 (d, J = 16, benzyl CH_2), 31.6 (ace-CH_2), 31.2 (ace-CH_2).

[Pt((*R,R*)-Me-DuPhos)(Ph)(PHPh(CH_2Ar))][PF_6] (17) A solution of secondary phosphine **Ph-11** (50 mg, 0.14 mmol) in 1 mL of THF was added to a solution of NH_4PF_6 (23 mg, 0.14 mmol, 1 equiv) in 1 mL of THF. To this mixture, a solution of Pt((*R,R*)-Me-Duphos)(Ph)(Cl) (87 mg, 0.14 mmol, 1 equiv) in 1 mL of THF was added; a white precipitate (NH_4Cl) formed immediately. Progress of the reaction was checked by ^{31}P NMR to ensure correct stoichiometry before further workup. The mixture was filtered through Celite. The solvent was pumped off, giving a white powder (158 mg, 104% yield of crude product which contained THF), which was pure according to ^{31}P NMR spectroscopy. This material was a 1.5:1 mixture of diastereomers. Recrystallization by vapor diffusion of pentane into a THF solution at -20 °C for 3 d gave white crystals. This reaction was also run with 0.632 g of Pt starting material to give 1.103 g of crude product (99% yield), which was pure according to ^{31}P NMR spectroscopy.

Anal. Calcd for $C_{43}H_{49}BrF_6P_4Pt$: C, 47.88; H, 4.58; Found: C, 48.10; H, 4.41. HRMS (m/z): calcd for $C_{43}H_{49}BrP_3Pt$ (M^+), 932.1878; found, 932.1877 (the mass spectrum was obtained for the triflate salt). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.6 (dd, J = 18, 8, J_{Pt-P} = 1601, A (major)), 65.4 (dd, J = 351, 8, J_{Pt-P} = 2639, B (minor)), 64.8 (dd, J = 18, 8, J_{Pt-P} = 1545, B), 64.7 (dd, J = 355, 8, J_{Pt-P} = 2640, A), -6.5 (dd, J = 351, 18, J_{Pt-P} = 2515, B), -9.9 (dd, J = 355, 18, J_{Pt-P} = 2515, A), -143.2 (septet, J = 712, PF_6). ^1H NMR ($CDCl_3$): δ 7.81-7.76 (m, 2H), 7.76-7.66 (m, 8H), 7.56-7.51 (t, J = 7, 1H), 7.46-7.41 (t, J = 8, 2H), 7.41-7.34 (m, 3H), 7.31-7.18 (m, 7H), 7.18-7.12 (m, 3H), 7.11-7.06 (m, 3H), 7.05-7.00 (m, 2H), 6.99-6.93 (m, 3H), 6.92 (d, J = 7, 1H), 6.36 (dd, J = 7, 3, 1H, Ar), 6.12 (dm, J_{P-H} = 373, 2H, PH), 4.62-4.50 (m, 1H, benzyl), 4.30 (dd, J = 15, 7, 1H, benzyl), 4.19-4.06 (m, 1H, benzyl), 3.40-3.23 (m, 8 H, ace CH_2), 3.17-3.06 (m, 1H, CH), 3.02-2.76 (m, 6H, 5 CH + 1 benzyl CH), 2.39-2.23 (m, 2H, CH_2), 2.22-1.99 (m, 5H, 1 CH + 2 CH_2), 1.92-1.52 (m, 7H, 1 CH + 3 CH_2), 1.45 (dd, J = 19, 7, 3H, CH_3), 1.43 (dd, J = 19, 7, 3H, CH_3), 1.30 (dd, J = 19, 7, 3H, CH_3), 1.21-1.12 (m, 2H, CH_2), 1.00 (dd, J = 19, 7, 3H, CH_3), 0.99 (dd, J = 16, 7, 3H, CH_3), 0.87 (dd, J = 17, 8, 3H, CH_3), 0.83-0.70 (m, 2H, CH_2), 0.55 (dd, J = 17, 7, 3H, CH_3), 0.52 (dd, J = 16, 7, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.2–150.9 (m, Ar, quat), 150.4–150.0 (m, Ar, quat), 149.6-149.4 (m, Ar, quat), 148.4 (d, J = 4, Ar, quat), 148.3 (Ar, quat), 148.1 (Ar, quat), 147.9 (d, J = 4, Ar, quat), 142.2 (d, J = 2, Ar, quat), 142.1 (d, J = 2, Ar, quat), 140.9–139.6 (m, Ar, quat), 139.9 (Ar), 138.0 (broad, Ar, quat), 136.9 (Ar), 135.5 (Ar), 135.0 (Ar), 134.6 (d, J = 2, Ar), 134.5 (d, J = 2, Ar), 134.2 (d, J = 7, Ar), 134.0 (d, J = 7, Ar), 134.1–133.5 (m, Ar), 133.3–132.9 (m, Ar), 132.6 (d, J = 2, Ar), 131.8 (d, J = 2, Ar), 130.4 (d, J = 5, Ar), 129.4 (d, J = 10, Ar), 129.2 (d, J = 10, Ar), 128.9 (d, J = 6, Ar), 128.1 (d, J = 3, Ar, quat), 127.6 (Ar, quat), 127.5 (Ar, quat), 125.8–125.3 (m, Ar, quat), 124.9 (Ar), 124.8 (Ar), 121.5 (Ar), 121.1 (Ar), 120.4 (d, J = 4, Ar), 119.8 (d, J = 3, Ar), 113.1 (d, J = 2, Ar-Br, quat, A), 112.9 (d, J = 2, Ar-Br, quat, B), 44.02 (d, J = 34, J_{Pt-C} = 40, CH), 44.00 (d, J = 35, J_{Pt-C} = 40, CH), 42.3 (d, J = 30, J_{Pt-C} = 15, CH), 42.2 (d, J = 30, J_{Pt-C} = 17, CH), 37.6 (d, J = 5, CH_2), 37.4 (d, J = 30, CH), 37.2 (d, J = 5, CH_2), 36.80-36.59 (m, overlapping, 4 CH_2), 36.5 (d, J = 30, CH), 35.59-35.44 (m, overlapping, 2 CH_2), 33.3 (d, J = 32, J_{Pt-C} = 33, CH), 32.9 (d, J = 33, J_{Pt-C} = 35, CH), 30.4 (ace-CH_2), 30.3 (ace-CH_2), 30.18 (ace-CH_2), 30.17 (ace-CH_2), 29.7 (dd, J = 30, 4, P-

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CH_2), 29.3 (d, J = 31, J_{Pt-C} = 31, P-CH_2), 17.5 (d, J = 7, J_{Pt-C} = 23, CH_3), 17.0 (d, J = 8, J_{Pt-C} = 22, CH_3), 15.9 (d, J = 5, J_{Pt-C} = 30, CH_3), 15.8 (d, J = 5, J_{Pt-C} = 30, CH_3), 14.7 (d, J = 2, CH_3), 14.5 (d, J = 2, CH_3), 14.3 (d, J = 2, CH_3), 13.8 (d, J = 2, CH_3).

Deprotonation of Secondary Phosphine Complex 17, Observation of the Phosphido Intermediate Pt((*R,R*)-Me-DuPhos)(Ph)(PPh(CH_2Ar)) (Ph-8) and its Cyclization to Yield [Pt((*R,R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][PF_6] (18) A solution of $NaOSiMe_3$ (5.2 mg, 0.046 mmol) in 0.4 mL of THF was added to a solution of cation **17** (50 mg, 0.046 mmol) in 1 mL of THF, to give a bright yellow solution. The ^{31}P NMR spectrum confirmed the formation of the two diastereomers of complex **Ph-8**.

$^{31}P\{^1H\}$ NMR (THF): δ 60.1 (d, J = 107, J_{Pt-P} = 1753, A), 59.4 (d, J = 100, J_{Pt-P} = 1761, B), 56.7 (J_{Pt-P} = 1738, A), 55.6 (J_{Pt-P} = 1700, B), -30.1 (d, J = 119, J_{Pt-P} = 881, A), -56.6 (d, J = 96, J_{Pt-P} = 852, B), -144.7 (septet, J = 711, PF_6). The diastereomer ratio was about 2:1 (A/B), and all the signals were broad.

The mixture was stirred at room temperature and white precipitate slowly formed. After stirring for 25 h, 44% of the phosphido complex cyclized to form **18** (^{31}P NMR integration). The reaction was done in 3 d and the solution became colorless. The ^{31}P NMR spectrum showed a 15:1 mixture of **18** and Ph-PyraPhos (**Ph-4**), plus Pt((*R,R*)-Me-DuPhos)(Ph)(Br) (**19**). A solution of NH_4PF_6 (7.5 mg, 1 equiv) in 0.5 mL of THF was added to remove bromide and convert this mixture to **18**. The THF was removed under vacuum and the solid residue was dissolved in 15 mL of CH_2Cl_2. The solution was washed with water. After drying with $MgSO_4$, removal of solvent gave 11 mg (24% yield) of white solid as a mixture of two diastereomers (2:1 ratio). See the ESI for more information on this reaction under different conditions.

Evaporation of a THF solution gave crystals of the major diastereomer **18a**, which co-crystallized with THF; it contained *R*-Ph-PyraPhos. See the ESI for synthesis of the enantiomer of the minor diastereomer, [Pt((*S,S*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][PF_6] (**18b'**), for which characterization data is included below.

[Pt((*R,R*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][PF_6] (18a) Anal. Calcd for $C_{43}H_{48}F_6P_4Pt{\cdot}C_4H_8O$: C, 52.76; H, 5.28; Found: C, 52.77; H, 5.29. HRMS (m/z): calcd for $C_{43}H_{48}P_3Pt$ (M^+), 852.2617; found, 852.2607. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 68.3 (dd, J = 15, 8, J_{Pt-P} = 1695), 63.1 (dd, J = 368, 8, J_{Pt-P} = 2607), 23.2 (dd, J = 368, 15, J_{Pt-P} = 2561), -143.2 (septet, J = 713, PF_6). ^{1}H NMR ($CDCl_3$): δ 7.83 (t, J = 7, 1H), 7.75-7.67 (m, 3H), 7.55 (t, J = 7, 1H), 7.44-7.27 (m, 8H), 7.06 (t, J = 7, J_{Pt-H} = 34, 1H), 7.03-6.97 (m, 1H), 6.95 (t, J = 7, J_{Pt-H} = 39, 1H), 6.81-6.72 (m, 2H), 4.24 (AB, J_{AB} = 18, J_{Pt-H} = 27, 1H, benzyl), 3.74 (ABX, J_{AB} = 18, J_{AX} = 9, J_{Pt-H} = 13, 1H, benzyl), 3.57-3.36 (m, 4 H, ace CH_2), 3.19-3.08 (m, 1H, CH), 2.90-2.74 (m, 3H, CH), 2.28-2.16 (m, 1H, CH_2), 2.07-1.92 (m, 3H, CH_2), 1.87 (dq, J = 13, 5, 1H, CH_2), 1.64 (dq, J = 13, 5, 1H, CH_2), 1.40 (dd, J = 19, 7, 3H, CH_3), 1.01 (dd, J = 16, 7, 3H, CH_3), 0.92 (dd, J = 20, 7, 3H, CH_3), 0.91 (dd, J = 17, 7, 3H, CH_3), 0.70 (tq, J = 11, 3, 1H, CH_2), 0.28 (dq, J = 13, 6, 1H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.0 (dd, J = 15, 8, Ar, quat), 149.5 (d, J = 2, Ar, quat), 149.3 (dd, J = 15, 8, Ar, quat), 144.0 (Ar, quat), 142.9-141.9 (m, Ar, quat), 140.6-140.3 (m, Ar), 140.2-139.9 (m, Ar, quat), 139.7 (d, J = 4, Ar, quat), 138.8 (d, J = 8, Ar, quat), 138.0 (dd, J = 16, 3, Ar, quat), 137.2 (Ar), 133.9 (dd, J = 14, 2, Ar), 133.3-133.0 (m, Ar), 132.8 (d, J = 5, Ar), 132.0 (d, J = 2, J_{Pt-C} = 19, Ar, quat), 131.14 (d, J = 7, Ar), 131.09 (Ar), 130.9 (d, J = 9, Ar), 129.2 (d, J = 11, Ar), 128.9 (d, J = 4, Ar), 128.3 (d, J = 4, J_{Pt-C} = 48, Ar), 125.4 (d, J = 8, Ar), 124.4 (Ar), 121.5 (Ar), 121.3 (d, J = 10, Ar), 44.4 (dd, J = 34, 2, J_{Pt-C} = 39, CH), 41.8 (d, J = 30, J_{Pt-C} = 18, CH), 38.8 (d, J = 28, J_{Pt-C} = 18, CH), 37.1 (J_{Pt-C} = 20, CH_2), 36.6 (d, J = 2, J_{Pt-C} = 31, CH_2), 35.5-35.3 (m, overlapping, 2 CH_2), 33.8 (d, J = 41, J_{Pt-C} = 40, CH_2 benzyl), 33.2 (d, J = 35, J_{Pt-C} = 35, CH), 31.8 (ace-CH_2), 31.2 (ace-CH_2), 17.9 (d, J = 10, J_{Pt-C} = 21, CH_3), 15.7 (d, J = 6, J_{Pt-C} = 28, CH_3), 14.6 (d, J = 3, CH_3), 14.2 (d, J = 2, CH_3).

[Pt((*S,S*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][PF_6] (18b') $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 68.6 (dd, J = 16, 7, J_{Pt-P} = 1685), 63.5 (dd, J = 367, 7, J_{Pt-P} = 2612), 23.5 (dd, J = 367, 16, J_{Pt-P} = 2578), -143.2 (septet, J = 712, PF_6). ^{1}H NMR ($CDCl_3$): δ 7.92 (dd, J = 7, 7, 1H), 7.80-7.75 (m, 1H), 7.75-7.69 (m, 2H), 7.45-7.41 (m, 1H), 7.41-7.37 (m, 4H), 7.31 (J_{Pt-H} = 16, 2H), 7.26-7.23 (m, 3H), 6.95 (t, J = 7, 1H), 6.69 (t, J = 7, 1H), 6.60 (dd, J = 7, 7, J_{Pt-H} = 41, 1H), 6.46 (dd, J = 7, 7, 1H), 4.05-3.94 (m, 2H, benzyl), 3.52-3.43 (m, 4 H, ace CH_2), 3.09-3.02 (m, 1H, CH), 2.98-2.87 (m, 2H, CH), 2.83-2.75 (m, 1H, CH), 2.48-2.37 (m, 2H, CH_2), 2.14-2.00 (m, 2H, CH_2), 1.98-1.87 (m, 1H, CH_2), 1.64 (dq, J = 13, 5, 1H, CH_2), 1.24 (dd, J = 19, 7, 3H, CH_3), 1.17 (dd, J = 16, 7, 3H, CH_3), 1.15 (1H, CH_2, overlapped), 1.12 (dd, J = 19, 7, 3H, CH_3), 0.90 (dd, J = 16, 7, 3H, CH_3), 0.60 (tq, J = 13, 4, 1H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.8 (d, J = 2, Ar, quat), 144.0 (Ar, quat), 140.2-139.9 (m, Ar), 138.8 (Ar, quat), 138.7 (Ar, quat), 138.6 (Ar, quat), 137.0 (Ar), 134.1 (d, J = 15, Ar), 133.4 (d, J = 3, Ar), 133.3-133.0 (m, Ar), 132.9 (d, J = 6, Ar), 132.5 (d, J = 8, Ar), 132.1 (J_{Pt-C} = 17, Ar), 132.0 (J_{Pt-C} = 16, Ar), 131.7 (d, J = 2, Ar), 129.9 (d, J = 6, J_{Pt-C} = 44, Ar), 129.4 (d, J = 11, Ar), 128.0 (d, J = 6, Ar), 125.4 (d, J = 7, Ar), 124.8 (Ar), 121.6 (Ar), 121.5 (Ar), 44.0 (d, J = 36, CH), 42.6 (d, J = 29, J_{Pt-C} = 16, CH), 39.5 (d, J = 27, J_{Pt-C} = 19, CH), 39.2-38.7 (m, CH_2 benzyl), 37.6 (J_{Pt-C} = 18, CH_2), 36.6 (J_{Pt-C} = 27, CH_2), 36.0 (d, J = 4, CH_2), 35.2 (d, J = 5, CH_2), 32.7 (d, J = 32, J_{Pt-C} = 32, CH), 31.9 (ace-CH_2), 31.2 (ace-CH_2), 18.0 (d, J = 9, CH_3), 15.5 (d, J = 5, J_{Pt-C} = 29, CH_3), 14.28 (CH_3), 14.27 (CH_3).

Reaction of Pt-Phosphido Complex Ph-8 with Silver Triflate Gave a Mixture of Products, Including Cyclometalated Cation 21 and Ph-PyraPhos Complex 18 A solution of cation **17** (30 mg, 0.028 mmol) in 0.3 mL of THF was treated with a solution of $NaOSiMe_3$ (4 mg, 0.04 mmol, 1.2 equiv) in 0.4 mL of THF to give a bright yellow solution of Pt-phosphido complex **Ph-8**. A solution of

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AgOTf (8 mg, 0.03 mmol, 1 equiv) in 0.4 mL of THF was added dropwise to the mixture, which immediately became dark. Within one minute, the mixture turned completely black and a precipitate formed. The mixture was either transferred into a NMR tube directly (A), or filtered through a Celite plug, which was washed with 0.5 mL of THF. The combined filtrates were transferred into a NMR tube (B). In both cases, the reaction was monitored by ^{31}P NMR spectroscopy, which showed that **Ph-8** had been consumed within minutes to yield intermediates with characteristic very broad signals near 0 ppm, as well as DuPhos resonances. These intermediates (see the ESI) decomposed over a few days to yield a mixture including cyclometalated cation **21** (major product), Ph-PyraPhos complex **18**, and an unidentified $[Pt(DuPhos)(phosphine)(X)]^+$ complex **22** ($^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.7 (d, J = 360, J_{Pt-P} = 2298), 67.8 (d, J = 13, J_{Pt-P} = 3338), 14.1 (dd, J = 360, 13, J_{Pt-P} = 2382)), in which the Pt-P coupling constant of 3338 Hz suggested the Pt–C bond had been broken. When the reaction mixture was filtered after addition of AgOTf (procedure B), less of **22** was formed.

Independent Synthesis of Cation 21 by Oxidative Addition of Phosphine 12 to Pt(0) A solution of phosphine **12** (43 mg, 0.10 mmol) in 2 mL of THF was added to a light brown solution of crude Pt((*R,R*)-Me-Duphos)(*trans*-stilbene) (68 mg, 0.10 mmol, 1 equiv) in 2 mL of THF. The mixture was stirred at room temperature for 6 h. The ^{31}P NMR spectrum showed full conversion of the Pt complex to product **21**, with about 10% of unreacted **12**. After addition of approximately 20 mg of extra crude Pt((*R,R*)-Me-Duphos)(*trans*-stilbene) in multiple portions, all the phosphine was consumed.

NH_4PF_6 (18 mg, 0.11 mmol, 1.1 equiv) was added to the reaction mixture. A white precipitate formed immediately. The mixture was filtered through a Celite plug to give a clear light brown solution, which was concentrated under vacuum and loaded onto a silica column. A mixture of ethyl acetate and pentane (2:1 ratio) was used as eluent (R_f = 0.2 in 3:1 ethyl acetate/pentane). After removal of the solvent under vacuum, the product was dissolved in CH_2Cl_2 and filtered through a Celite plug. Removal of CH_2Cl_2 under vacuum gave 63 mg (64% yield) of light yellow solid, which contained less than 2% impurities, as indicated by NMR spectra.

In a similar reaction starting with 46 mg (0.11 mmol) of phosphine **12**, after the reaction was completed, 23 mg of NH_4PF_6 (0.14 mmol, 1.3 equiv) was added to the mixture and a white precipitate formed immediately. The mixture was filtered through a Celite plug to give a clear light brown solution. Removal of the solvent under vacuum gave a light brown residue, which was washed with 20 mL of ether. A solution of the residue in 10 mL of CH_2Cl_2 was washed with water (2 x 10 mL), concentrated under vacuum, loaded onto a silica column, and eluted with 3:1 ethyl acetate/pentane. Small analytically pure light yellow X-ray quality crystals formed from the eluent in 1 h.

Anal. Calcd for $C_{43}H_{48}F_6P_4Pt$: C, 51.76; H, 4.85; Found: C, 51.36; H, 4.57. HRMS (m/z): calcd for $C_{43}H_{48}P_3Pt$ (M^+), 852.2617; found, 852.2629. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.9 (dd, *J* = 356, 8, J_{Pt-P} = 2672), 62.8 (dd, *J* = 13, 8, J_{Pt-P} = 1762), 7.9 (dd, *J* = 356, 13, J_{Pt-P} = 2566), -144.3 (septet, *J* = 712, PF_6). ^{1}H NMR ($CDCl_3$): δ 7.80 (dd, *J* = 7, 7, 1H), 7.74 (dd, *J* = 7, 7, 1H), 7.69-7.64 (m, 2H), 7.58 (dd, *J* = 7, 7, J_{Pt-H} = 42, 1H), 7.56-7.53 (m, 2H), 7.52-7.48 (m, 1H), 7.48-7.40 (br, m, 2H), 7.30-7.25 (m, 3H), 7.14 (t, *J* = 7, 1H), 7.10 (d, *J* = 7, 1H), 7.04-6.99 (m, 3H), 4.48 (dd, *J* = 16, 7, J_{Pt-H} = 30, 1H, benzyl CH_2), 3.73 (ddd, *J* = 16, 15, 4, J_{Pt-H} = 68, 1H, benzyl CH_2), 3.57-3.46 (m, 1H, CH), 3.28-3.08 (m, 4H, ace CH_2), 2.90-2.80 (m, 1H, CH), 2.68-2.56 (m, 1H, CH), 2.25-2.10 (m, 2H, CH_2), 1.97-1.80 (m, 2H, CH_2), 1.73-1.62 (m, 2H, CH_2), 1.57-1.47 (m, 1H, CH, overlapped), 1.51 (dd, *J* = 19, 7, 3H, CH_3), 1.03 (dd, *J* = 16, 7, 3H, CH_3), 0.86 (dd, *J* = 20, 7, 3H, CH_3), 0.78-0.70 (m, 1H, CH_2), 0.59 (dd, *J* = 16, 7, 3H, CH_3), 0.44 (qm, *J* = 13, 1H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.9 (Ar, quat), 143.5 (Ar, quat), 141.9 (ddd, *J* = 42, 30, 5, Ar, quat), 140.1 (d, *J* = 5, Ar, quat), 140.0 (ddd, *J* = 44, 31, 3, Ar, quat), 138.4 (ddd, *J* = 89, 18, 5, Ar, quat), 136.7 (d, *J* = 9, Ar), 135.0-134.5 (broad, Ar), 134.7 (apparent t, *J* = 5, Ar, quat, overlapped), 134.4 (dd, *J* = 12, 4, Ar, quat), 133.3 (dd, *J* = 13, 1, Ar), 133.1 (dt, *J* = 13, 2, Ar), 132.6 (dd, *J* = 6, 2, Ar), 132.5 (d, *J* = 5, Ar), 131.8 (d, *J* = 2, Ar), 131.5 (d, *J* = 2, Ar), 129.4 (d, *J* = 10, Ar), 129.2 (d, *J* = 10, Ar), 128.3 (d, *J* = 12, Ar), 128.0 (d, *J* = 4, Ar, quat), 126.8-126.6 (m, Ar, quat), 120.1 (d, *J* = 6, J_{Pt-C} = 49, Ar), 118.4 (Ar), 42.3 (d, *J* = 35, J_{Pt-C} = 51, CH), 41.6 (d, *J* = 31, J_{Pt-C} = 19, CH), 36.2 (d, *J* = 3, J_{Pt-C} = 30, CH_2), 36.1 (J_{Pt-C} = 20, CH_2), 36.0 (d, *J* = 4, CH_2), 35.3 (d, *J* = 4, CH_2), 34.0 (d, *J* = 27, J_{Pt-C} = 16, CH), 30.0 (ace-CH_2), 29.8 (ace-CH_2), 29.6 (d, *J* = 32, CH), 29.4 (d, *J* = 39, benzyl CH_2), 19.5 (d, *J* = 9, J_{Pt-C} = 27, CH_3), 17.4 (d, *J* = 6, J_{Pt-C} = 42, CH_3), 13.8 (CH_3), 13.5 (d, *J* = 2, CH_3).

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Notes and references
[a] 6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States
[b] Department of Chemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093, United States

Electronic Supplementary Information (ESI) available: Additional experimental details (text, tables, and NMR spectra). X-ray crystallographic data has been deposited (CCDC numbers 1047184-1047193) See DOI: 10.1039/b000000x/

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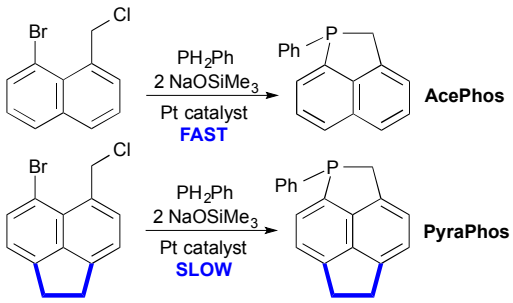
Synthesis of a Phosphapyracene via Metal-Mediated Cyclization: Structural and Reactivity Effects of Acenaphthene Precursors

Ge Wang,[a] Marites A. Guino-o,[a] David S. Glueck,[a]* James A. Golen,[b] Christopher J. A. Daley,[b] and Arnold L. Rheingold[b]

Graphical and text abstract



A small structural change (naphthalene to acenaphthene) had large effects on reactivity, slowing Pt-mediated phosphination/cyclization; the new heterocycle PyraPhos was prepared with a simple Cu catalyst.